

Microwave irradiation effects on the structure, viscosity, thermal properties and lubricity of soybean oil[☆]

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Abstract

Soybean oil is a highly valuable agricultural commodity for the United States. To further add value to soybean oil, chemical and physical modifications, as well as additives, have been extensively used to change the oil characteristics and properties, broadening the potential industrial applications. Heat treatments such as heat-bodding have been implemented to change soybean oil properties, but no research has studied the effects of microwave-irradiation on soybean oil structure and properties.

Soybean oil (SBO) was heat-bodded (HB) or microwave-irradiated (MI). HB and MI (200–250 °C for 20–60 min) oil had similar Gardner bubble viscosity (B–C range). SBO that was HB or MI had increased viscosity compared with untreated SBO. ¹H NMR analysis showed no oxidation occurred for all treatments. However, HB and MI oil formed a cyclic ring structure with polymerization that most likely contributed to the increased viscosity. Pour point decreased from –9 °C for the untreated SBO, –15 °C for the HB, and –18 °C for the MI despite viscosity increases. Pour point anomaly is likely due to triacylglyceride cyclic ring formation. Pressurized DSC analysis showed higher oxidative stability for HB oil with even higher stability for MI oil. Compared with untreated SBO, HB and MI oil increased friction coefficient and decreased film percentage, whereas MI oil tended to leave larger wear scratches on the ball and disk during friction measurements. MI oil improved SBO cold-flow behavior, but reduced its potential as a lubricant. © 2006 Elsevier B.V. All rights reserved.

Keywords: Soybean oil; Microwave irradiation; Structure; Viscosity; Pour point; Lubricant; Oxidative stability

1. Introduction

Refined soybean oil has a large number of industrial applications including anti-corrosion agent, biodiesel, lubricants, anti-static agent, fungicides, pesticides, caulking compounds, electrical insulation, dust control agent, disinfectants, epoxys, linoleum backing, and paints (Erhan et al., 2002a,b). Heat treatments such as heat-bodding have been implemented to change soybean oil properties (Kenar et al., 2002), but no research has

[☆] Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that may also be suitable.

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studied the effects of microwave-irradiation on soybean oil structure and properties.

Because microwave heating is a common domestic appliance used for cooking, the vast majority of studies researching the effects of microwave-irradiation on oil structure and properties have focused on the changes in the lipids of the food itself. Many other studies have exposed seed crops to microwave irradiation prior to any extraction processes, but few studies have focused on the changes in structure and properties of microwave-irradiated purified oil. The viscosity and *trans*-isomer content of virgin olive, olive, sunflower, and high-oleic sunflower oils, as well as lard, increased more when microwave-heated than with conventional heating (Albi et al., 1997a). Microwave irradiation of the same lipids greatly increased acid value, peroxide value, dielectric point of polar compounds than with untreated and conventional heating (Albi et al., 1997b). Peroxide value of microwave-irradiated corn oil increased during the first 6 min of heating, but subsequently decreased due to the instability of hydroperoxides at high temperature (Vieira and Regitano-d'Arce, 1999). Peroxide and iodine values decreased, whereas free fatty acid content for corn and soybean oil increased with microwave-irradiation (Tan et al., 2001). Accelerated oxidation of microwave-irradiated rapeseed, soybean and safflower oils was reported (Yoshida and Takagi, 1999) and oxidative rate increased with higher levels of unsaturated fatty acids (Yoshida, 1993). Microwave-irradiated oils have higher polyphenol content than oils heated conventionally (Albi et al., 1997b; Brenes et al., 2002).

Vegetable oil-based lubricants have increasingly gained interest because of their biodegradability minimizes environmental impact. Recently, this interest has accelerated due to the uncertainty in the supply and cost of petroleum crude oil. Vegetable oil-based lubricants have excellent lubricity, biodegradability, superior viscosity–temperature characteristics, and low evaporation loss, but they need improvement in thermo-oxidative stability and cold-flow behavior. Pour point, the lowest temperature at which the oil still shows movement, is a useful measurement of cold-flow behavior. Improvement in oxidative stability and lower pour point of soybean oil at colder temperatures have been carried out by chemical modification (Hwang and Erhan, 2001; Isbell et al., 2001; Cermak and Isbell, 2002; Erhan et al., 2002a; Adhvaryu et al., 2005) and use of additives (Asadauskas and Erhan, 1999; Sharma et al., 2005). No studies have investigated changes in pour point after microwave irradiation of vegetable oil.

In addition to the limited research on changes in lipids of microwave irradiation of purified oils, the oil lubrication

properties after microwave irradiation has not been researched. The properties of microwave irradiated soybean oil were determined at various temperature–time combinations. The sophisticated Ethos 1600 microwave was used that can accurately maintain temperature, wattage, power, and pressure. The structure, viscosity, thermal properties, and lubricity of the microwave-irradiated oil was analyzed and compared with untreated and heat-bodied soybean oil.

2. Experimental procedure

2.1. Materials

Alkali refined soybean oil was obtained from ADM Packaged Oils, Decatur, IL.

2.2. Heat bodying

Soybean oil heated at $305 \pm 3^\circ\text{C}$ under a nitrogen purge as described previously (Wang and Erhan, 1999) for a range of time intervals producing oil with a viscosity determined by the Gardner Bubble Viscometer (ASTM D-1545-63, Paul Gardner Co., Inc., Pompano Beach, FL) to be in the range of A–B, B–C, T–U and Z₁–Z₂, where A is the minimum and Z is the maximum viscosity.

2.3. Microwave irradiation

A sophisticated microwave (Ethos 1600, Milestone Inc., Monroe, CT) was used to microwave irradiate about 20 g of soybean oil in a sealed 100 ml perfluoroalkoxy Teflon[®] reactor vessel (product code 45111T). The sample was heated at 150°C for 10 min, or 200°C for 20, 30 or 60 min, or 250°C for 30 or 60 min. All the data presented here were the average value of 3–5 independent experiments over 7-month periods. Each reaction vessel included one Weflon[™] stirrer bar (32 mm \times 9 mm, product code 86106), one Weflon[™] solid, cylindrical heating bar (18 mm \times 3 mm, W000520) and two Weflon[™] heating buttons (18 mm diameter, W01703) and a stirring rate of 317 rpm used.

2.4. NMR analysis

All ^1H spectra were recorded quantitatively with a Bruker ARX-500 spectrometer (Bruker, Rheinstetten, Germany) at a frequency of 500 MHz and a 5 mm dual probe. For the ^1H experiments, sample solutions were prepared in deuterated chloroform (CDCl_3 , 99.8% D) in 15% (v/v) concentrations. Proton NMR spectra were obtained on 16 co-added FIDs with a delay time of 1 s. To

determine the precision of estimation of area %, a spectrum of the oil sample was recorded three times under similar conditions, with each spectrum integrated three times.

2.5. Pressurized differential scanning calorimetry

Thermal properties of the soybean oils were determined with a PC-controlled DSC 2910 from TA Instruments (New Castle, DE). The instrument has a maximum sensitivity of 5 mV cm^{-1} and temperature sensitivity of 0.2 mV cm^{-1} . A 1.5–2.0 mg sample was placed in a hermetically sealed aluminum pan with a pinhole lid for interaction of the sample with the reactant gas (dry air). The controlled diffusion of the gas through the hole greatly restricts the volatilization of the oil while still allowing for saturation of the liquid phase with air. A film thickness of less than 1 mm was required to ensure proper oil–air interaction and to eliminate any discrepancy in the result due to gas diffusion limitations. The module was first temperature calibrated using the melting point of indium metal (156.6°C) at a $10^\circ\text{C min}^{-1}$ heating rate. Dry air was pressurized in the module at a constant pressure of 1379 kPa and a scanning rate of $10^\circ\text{C min}^{-1}$ was used throughout the experiment. The onset temperature was calculated from the exotherm in each case. Data presented in Table 1 for onset temperature measurement is the average of three independent experiments under identical conditions.

2.6. Pour point

Pour point of the microwave-irradiated soybean oils was measured by following the ASTM D97 (ASTM, 2000) method. A $150 \mu\text{l}$ sample was placed in a pour,

Table 1

Pour point and onset temperature of soybean oil of unmodified (SBO), heat-bodied (HBSBO (B–C)) or microwaved at 150, 200, or 250°C for times varying from 10 to 60 min

Oil	Pour point ^a ($^\circ\text{C}$)	Onset temperature ^b ($^\circ\text{C}$)
SBO	–9	132.1
HBSBO (B–C)	–15	155.7
MISBO 150/10	–18	139.3
MISBO 200/20	–18	160.7
MISBO 200/30	–18	160.1
MISBO 200/60	–18	157.7
MISBO 250/30	–18	160.9
MISBO 250/60	–18	161.7

^a Average value of five independent measurements over 7-day period. The temperature repeatability was $\pm 0.7^\circ\text{C}$.

^b Average value of three independent experiments. Error of estimate ± 1.0 .

cloud and freeze point analyzer (model PSA-70S, Phase Technology, Richmond, BC, Canada). Pour point data presented is an average of five independent measurements performed over a 7-day period.

2.7. Friction measurements

Lubrication properties of microwave-irradiated soybean oil were measured using a high-frequency reciprocating rig (HFRR) (Model HFR2, PCS Instruments, London, England). In the procedure, the ball rubs against a disk for 75 min at 50 strokes s^{-1} where the length of each stroke is 1 mm, and at a temperature of 60°C . The test load between ball and disk is 200 g. The average scar was calculated by microscopically measuring the length and width (three times for each) of the scar on the ball at end of test and obtaining the average of these two dimensions. The diameter of the circular wear scar left on the disk was also measured using a scanning electron microscope (JOEL model 6400 V, Tokyo, Japan). The results presented from the friction test are average value of three repeated experiments. The test method is extremely accurate and highly repeatable and any variance above 0.1% was rarely noticed. Post-test, the disks were carefully soaked to remove the excess oil left on the disk surface. Care was taken not to dislodge the metallic debris from the wear track or on the edges of the track. With a few exceptions, lubricity tests were conducted only in triplicate, due to cost and time associated with testing of samples.

2.8. Viscosity measurements

The viscosity of heat-bodied soybean oils was estimated using a Gardner Bubble Viscometer (Paul Gardner Co., Inc., Pompano Beach, FL), Class G, 10.65 mm i.d., following ASTM method D1545-63. The kinematic viscosity of heat-bodied and microwave-irradiated soybean oils was measured using Cannon–Fenske calibrated viscometers (Cannon Instrument Co., State College, PA) in a Cannon temperature bath (CT-1000) at 40°C . According to ASTM standard method D445-95 (Annual Book of ASTM Standards, 2000). The viscosities obtained are average values of 2–3 determinations and the precision is within the limits of ASTM method specification.

3. Results and discussion

To evaluate whether microwave irradiation of soybean oil provides viscosity and lubricity characteristics that differ from other heat processes, heat-bodied and MI soybean oils were produced over a range of viscosities.

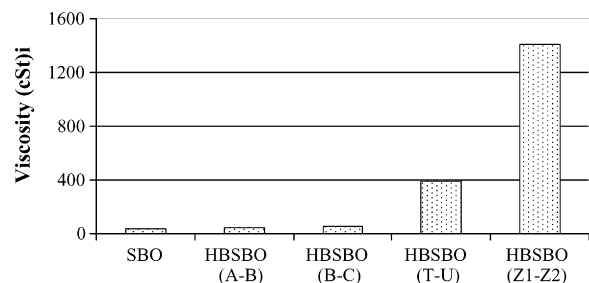


Fig. 1. Kinematic viscosity of untreated soybean oil (SBO) and heat-bodied soybean oil (HBSBO) for various durations measured using a Cannon–Fenske calibrated viscometer at 40 °C.

Heat-bodding involves heating the soybean oil at high temperatures in the presence of nitrogen. The duration of heating was increased further to polymerize the oil, and thereby increasing viscosity. The kinematic viscosities obtained from heat-bodding are shown in Fig. 1.

The viscosities of the untreated and microwave-irradiated soybean oil are shown in Fig. 2. The viscosity of 35.4 cSt that we report for untreated soybean oil is similar to that reported previously (Isbell et al., 2001). Increasing the microwave temperature to 200 °C and duration to 20 min increased viscosity over the oil microwave-irradiated at 150 °C for 10 min. Further increasing the temperature (250 °C) and duration (20–60 min), to the highest temperature, resulted in only a slight increase in viscosity. Increased viscosity after microwave-irradiation has previously been reported for olive and sunflower oils (Albi et al., 1997a). Heat-bodied soybean oil with Gardner bubble viscosity range of B–C (HBSBO (B–C)) had similar viscosity to that of all microwave-irradiated soybean oil treatments studied. Thus, the HBSBO (B–C) was selected to compare differences between heat-bodied and microwave-irradiated oil.

The ^1H NMR spectra of SBO, HBSBO (B–C), and SBO (250/30) are shown in Fig. 3. Analysis of these

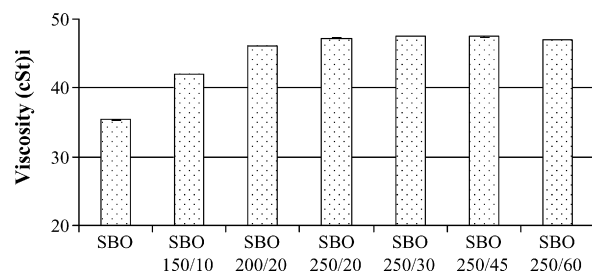


Fig. 2. Kinematic viscosity of untreated soybean oil (SBO) and soybean oil microwave-irradiated for various temperatures and durations using a Cannon–Fenske calibrated viscometer at 40 °C. The first number refers to the microwave temperature (°C) and the second number to the treatment microwave duration (min).

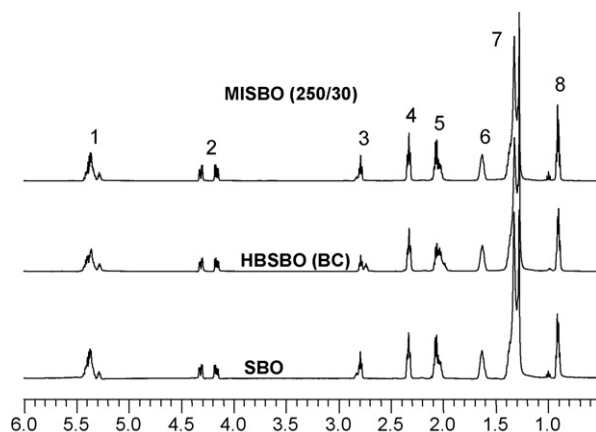


Fig. 3. Partial ^1H NMR spectra of soybean oil that has been untreated (SBO), heat-bodied with Gardner viscosity in the B–C range (HBSBO (B–C)) or microwave-irradiated at 250 °C for 30 min (MISBO 250/30).

spectra shows that similar products are obtained in heat-bodding and microwave irradiation reactions. No oxidized products were formed as indicated by the absence of any extra peaks. The backbone of triglyceride structure is intact, based on observations of retention of NMR peaks of backbone glycerol structure in heat-bodied and microwave-irradiated oils. These are peak 2 at 4.12–4.36 ppm for CH_2 proton of $-\text{CH}_2-\text{CH}-\text{CH}_2-$ glycerol backbone, and peak 4 at 2.28–2.39 ppm for CH_2 protons α to $>\text{C}=\text{O}$. The retention of the triacylglycerol backbone is important for maintaining high biodegradability. Other ^1H NMR peaks that are common in SBO, HBSBO (B–C), and SBO (250/30) are peak 6 at 1.57–1.70 ppm for CH_2 protons β to $>\text{C}=\text{O}$, peak 7 at 1.22–1.46 ppm for all other CH_2 protons and peak 8 at 0.86–0.95 ppm for terminal CH_3 protons.

Quantitative data obtained from the eight peaks observed in ^1H NMR spectra of the different oils are presented in Fig. 4. These values are computed using a reference value of four protons for peak 2 at 4.12–4.36 ppm corresponding to four CH_2 protons of $-\text{CH}_2-\text{CH}-\text{CH}_2-$ in the glycerol backbone of triacylglycerol structure. The percentage area of peak 1 at 5.24–5.46 ppm ($-\text{CH}-$ protons of double bonds) decreased in HBSBO (B–C) and SBO (250/30) as shown in Fig. 4. The decrease in double bonds was further confirmed by the decrease in percentage area of peak 3 at 2.75–2.85 ppm ($-\text{CH}_2-$ protons of bis-allylic) and peak 5 at 1.97–2.14 ppm ($-\text{CH}_2-$ protons of allylic). This shows that during heat-bodding or microwave irradiation, these double bonds are reacting to form cyclic structures (Wang and Erhan, 1999) by the Diels–Alder reaction resulting in dimerization of triglyceride molecules. At the temperature of heat-bodding, the double bonds migrate and conjugated dienes are formed,

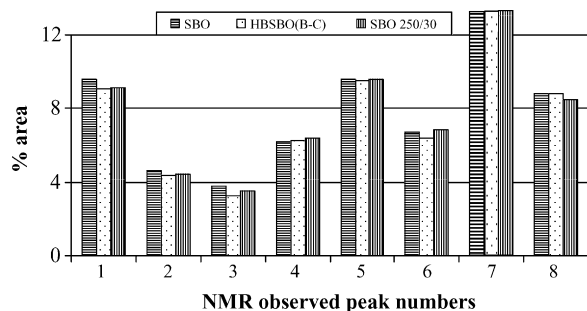


Fig. 4. Percentage peak area of each of the eight observed peaks from ^1H NMR spectra for soybean oil that was untreated (SBO), heat-bodied with Gardner viscosity in the B–C range (HBSBO (B–C)) or microwave-irradiated at 250°C for 30 min (MISBO 250/30). (The area % of peak 7 is 50.72, 52.24, and 51.54 for SBO, HBSBO (B–C), and SBO 250/30 respectively.)

which is a reactive form for heat-bodding. These conjugated dienes add readily to active double bonds to form a six-membered ring containing one double bond, that can further add to a conjugated group to form a second ring. This ring formation leads to a bond between two triacylglycerols and results in the formation of larger molecules as more and more triacylglycerols combine. This polymerization process often leads to increased oil viscosity making the heat-bodied or microwave-irradiated oils potential candidates for hydraulic fluids and gear oils.

The pour points of soybean oil that was untreated, heat-bodied HBSBO (B–C), or microwave-irradiated are listed in Table 1. The pour point of -9°C that we report for untreated soybean oil agrees with previous studies (Asadauskas and Erhan, 1999). Pour point is the lowest temperature at which the oil still shows movement. Pour point has always been assumed to increase with viscosity (Smith, 1979). However, the most striking observation of this study was that both HBSBO (B–C) and in particular microwave-irradiated soybean oil had suppressed pour points despite increased viscosity compared with untreated soybean oil. The depression in pour point by converting *trans* unsaturation to *cis* unsaturation has been reported (Asadauskas and Erhan, 1999), but this can not be occurring in *trans*-fatty acid-free soybean oil. Microwave-irradiation would have been expected to oxidize the oil, and change the oil structure in a manner that increased viscosity while lowering pour point. However, the oxidized oil would be expected to have higher molecular weight that favors higher temperatures of solidification (Hagemann, 1988; Larsson, 1994). Based on our ^1H NMR results, the oxidation of soybean oil while microwave-irradiated is unlikely to have occurred. The ^1H NMR analysis suggests that

the polymerization of cyclic triacylglyceride rings during heat-bodding and microwave irradiation could be contributing to an unusual phenomenon of increased viscosity, but depressed pour point.

Vegetable oil-based lubricants have been reported to have problems of cloudiness, precipitation, poor flowability, poor pumpability, and solidification at -15°C (Rhee et al., 1995). Incorporating pour point depressants into oils or modification of oils has been utilized to suppress the undesirable formation of large crystals during solidification (Dunn and Bagby, 1995; Asadauskas and Erhan, 1999; Hwang and Erhan, 2001). However, our results suggest that pour point could also be lowered by microwave irradiation. Because vibrations can affect crystallization thermodynamics (Greaves et al., 2005), the stirring during microwave irradiation of soybean oils could have disrupted crystallization.

Pressurized differential scanning calorimetry (PDSC) is an effective way to measure the oxidative tendency of vegetable oils in an accelerated mode. At high air pressure (1379 kPa), O_2 concentration is in excess and equilibrated with sample, thus effectively eliminating any inconsistency due to changes in O_2 concentration and egress rate of volatile degradation product. PDSC analysis of untreated soybean as well as HBSBO (B–C), or soybean oil microwave-irradiated for various temperature and time combinations ranging from 150 to 250°C and 10 to 60 min are shown in Table 1. The onset temperature (T_o) of the exothermic thermal transition for HBSBO (B–C) is considerably elevated compared with the untreated soybean oil indicating improved oxidative stability. Soybean oil microwave-irradiated at 150°C for 10 min also had elevated T_o than the untreated soybean oil, but was considerably lower than the HBSBO (B–C). However, soybean oil microwave-irradiated at 200°C for 20–60 min or 250°C for 30–60 min had higher T_o than HBSBO (B–C) indicating enhanced oxidative stability than the heat-bodied oil that has comparable viscosity. Enhanced oxidative stability is most likely due to the decrease in double bonds and the formation of cyclic triacylglyceride ring structures. Microwave irradiation most likely produced few free fatty acids because they have been reported to reduce greatly the oxidative stability of microwave-irradiated soybean oil (Yoshida et al., 1992a,b). The presence of intact triglycerides has been confirmed by ^1H NMR. In contrast to our findings, Albi et al. (1997b) reported partial hydrolytic degradation when olive oil, sunflower oil, and lard were microwave-irradiated than the untreated or conventional oven heating. However, they used a microwave oven that is used in the household kitchen and does not provide accurate control over radiation.

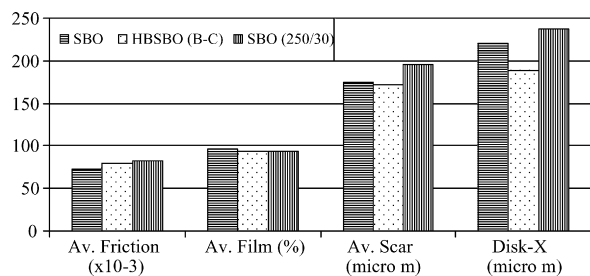


Fig. 5. Coefficient of friction (av. friction) divided by a thousand, average film (%), average wear scar on ball from high-frequency reciprocating rig (HFRR) analysis (av. scar in μm) and average wear scratch on disk that ball rubbed against during HFRR analysis (Disk-X in μm) for soybean oil that was untreated (SBO), heat-bodied with Gardner viscosity in the B–C range (HBSBO (B–C)) or microwave-irradiated at 250 °C for 30 min (MISBO 250/30).

The high-frequency reciprocating rig (HFRR) is a method to determine the lubricity or the ability of a fluid to affect friction between, and wear to surfaces in relative motion under load. The average coefficient of friction (COF), average film percentage, average circular wear scar diameter and average width of wear track on disk for untreated soybean oil, HBSBO (B–C) and microwave-irradiated soybean oil are shown in Fig. 5 using HFRR. The average COF was increased when soybean oil was heat-bodied and greater friction was experienced with soybean oil that had been microwave-irradiated at 250 °C for 30 min. Microwave irradiation appears to have altered oil structure in a manner that reduces the ability of the oil to form a thin lubricating film at the point of metal contact. Polar functional groups in triacylglycerol molecules make physical and chemical interaction with metallic surfaces under high load and sliding contact (Biresaw et al., 2002). The molecular polar groups are the point of attachment to metal, with the non-polar end forming a molecular layer separating the rubbing surfaces (Adhvaryu et al., 2004). Because there is no increase in polar functional groups on heat-treating or microwave irradiation, no lowering in friction is expected. Dimerization of triacylglycerol molecules as a result of heat treating or microwave irradiation may lead to a decrease in effective polar groups because of the configuration of the dimerized molecule. This leads to less effective adsorption of the oil on metal surface, which can explain increased friction or reduced lubricity after soybean oil has been microwave-irradiated or heat treated. Additionally, microwave-irradiation may have degraded polar functional groups, further reducing the oil lubricity. Despite the higher friction for microwave-irradiated oil, only a slight decrease was present in the average lubricant film percentage.

The wear track width made with HBSBO (B–C) was lower than the untreated soybean oil despite having higher friction (Fig. 5). However, microwave-irradiated soybean oil that had higher friction than untreated oil had a wider wear track. Little difference in the size of the scar was observed on ball between untreated soybean oil and HBSBO (B–C), but microwave-irradiated oil had a larger scar on ball.

Our results demonstrate that there is a difference between the heat treatments of heat-bodying and microwave irradiation on the oil characteristics. These differences may be attributed to the heat produced. Albi et al. (1997b) reported that microwave heating altered olive and sunflower oil characteristics compared with conventional heating, but oil exposed to microwave energy without allowing temperature to rise above 40 °C had no alterations.

4. Conclusions

Heat-bodying (HB) and microwave irradiation (MI) increased the viscosity of soybean oil. Pressurized differential scanning calorimetry showed that the HB considerably improved oxidative stability over the untreated soybean oil, and oil exposed to MI had greater oxidative stability than HB. The most noteworthy finding of this study was that HB, and to a greater extent MI, lowered the pour point considerably compared with untreated soybean oil despite having an increase in viscosity. ¹H NMR analysis showed no occurrence of oxidation regardless of treatment and that the pour point anomaly is most likely the result of the formation of triacylglyceride cyclic ring structures that caused an increase in viscosity. Greater friction was observed for oils treated by HB and MI than the untreated and particularly MI, which left greater wear scratches on the ball and disk surfaces used for lubricity studies. Microwave irradiation shows promise to improve the cold-flow behavior of soybean oil, but MI treatment will not produce superior vegetable oil-based lubricants.

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